

**Progress Report**

**NASA Research Grant NSG-217/33-016-009 to New York University**

**Nitric Oxide Photolysis**

**Period** September 1, 1965 to February 28, 1966

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**Submitted to:** Office of Grants and Research Contracts  
Attention: Code SC  
National Aeronautics and Space Administration  
Washington, D. C. 20546

**N66-83843**

FACILITY FORM 602	(ACCESSION NUMBER)	(THRU)
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	(PAGES)	more
	CR 94913	(CODE)
	(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

Since the absence of  $\text{N}_2\text{O}$  among the products of photolysis of  $\text{NO}$  in a static system at 1470 Å had been clearly demonstrated by us by careful gas chromatographic analysis, two alternatives are presented: (1) no  $\text{N}_2\text{O}$  production is possible or (2)  $\text{N}_2\text{O}$  production is possible but, in the static system,  $\text{N}_2\text{O}$  undergoes subsequent decomposition and does not accumulate appreciably. Against alternative (1), there is Kistiakowsky's evidence of reaction between  $\text{N}$  atoms and  $\text{NO}_2$  to produce  $\text{N}_2\text{O}$  and, more recently, Rice and Wunderlich's evidence of reaction of excited  $\text{NO}^*$  with  $\text{NO}_2$  to produce  $\text{N}_2\text{O}$ . Kistiakowsky's evidence is not unequivocal, depending on the validity of mass-spectral analysis, which we have shown unreliable. Rice's evidence is experimental and too internally consistent not to be reliable. The postulated reaction, though conceivable for the conditions of his system, need not necessarily occur in ours with a wavelength of 1470 Å as against 3655 Å in his. The excited states of  $\text{NO}$  are so numerous that Rice's postulated excited  $\text{N}_2\text{O}_3^*$  might not be possible with 1470 Å radiation.

To solve the problem unequivocally, since  $\text{N}_2\text{O}$  if present at all is a secondary product, not pertinent to the major  $\text{NO}$  photolysis into  $\text{N}_2$  and  $\text{NO}_2$ , an attempt must be made to determine the life of the  $\text{N}_2\text{O}$  in the system. To this end, photolysis of  $\text{NO}$  in a flow system was initiated. The results serve two purposes: (1) corroboration of the static system results on  $\alpha$  quantum yields and (2) demonstration of  $\text{N}_2\text{O}$  as a secondary intermediate.

The static system exposures having been of 15 to 30 min. duration, flow runs were begun with about 10 min. contact time, actually 9.75 min., which could be reduced, using the given flowmeter to 0.73 min. In this range of contact times, using the procedure developed for the analysis of products from static runs, namely, partial preparation by fractionation followed by GC analysis, data have been collected but no  $\text{N}_2\text{O}$  has been found. Since the absorption of 1470 Å radiation is high and absorption is complete in a small thickness, by reducing the size of the reaction vessel, using the same flowmeter, the contact time has been further reduced to 0.2 min. No  $\text{N}_2\text{O}$  has been found. With a new flowmeter the contact time is being further reduced, first to about  $10^{-2}$  min and possibly further. The latter possibility may depend on purely analytical precision. With these high flow rates, the total amount of photolysis is decreasing. The possibility of any effective build-up of  $\text{NO}_2$  is therefore likewise decreasing and a limit may thereby be set to  $\text{N}_2\text{O}$  production. Alternatively, the

absence of  $\text{N}_2\text{O}$  may simply mean that the reaction:  $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$  because of the high  $\text{NO}$  pressure is so fast, that the slower reaction of  $\text{N} + \text{NO}_2 \rightarrow \text{N}_2\text{O} + \text{O}$  just cannot compete.

If no  $\text{N}_2\text{O}$  is found even at very slow flow rates, the effect of traces of oxygen in the  $\text{NO}$ , which would give added  $\text{NO}_2$  in the system, will be investigated.